

SELECTIVITY CONTROL UTILIZING ACTIVATION ENERGY DIFFERENCES HYDROGENATION OF CO

N. A. Bhore, K. B. Bischoff, W. H. Manogue, and G. A. Mills
Center for Catalytic Science and Technology
Department of Chemical Engineering
University of Delaware
Newark, DE 19716

INTRODUCTION

Multifunctional catalysts offer important opportunities for scientific advances and industrial applications since they are able to activate different molecular species simultaneously. Of critical interest is the molecular structures of the catalyst responsible for such multiple activations, how the activated species interact, and how the reaction dynamics control activity and selectivity.

Hydrogenation of carbon monoxide is a widely studied reaction with many practical applications. The catalytic performances of supported Rh catalysts for CO hydrogenation are very dependent on the support and added modifiers (1-11). Of particular interest is the novel Rh-Mo/Al₂O₃ catalyst system which displays exceptionally high activity for CO hydrogenation and high selectivity for formation of oxygenates.

Kinetic and characterization tests were carried out using catalysts consisting of Rh on Al₂O₃ and on TiO₂ with various amounts of added molybdena. The results are discussed in terms of selectivity enhancement by utilizing differences in activation energies for selective and non-selective reactions. Reaction mechanisms are discussed in terms of a dual-site functionality with implications for design of improved catalysts.

EXPERIMENTAL

Catalysts of composition shown in Table 1 were prepared by impregnation. All contain a nominal 3% Rh from rhodium nitrate solution. The alumina was Catapal and the titania Degussa P-25. Those containing molybdena were prepared in stages. The support was first impregnated with ammonium molybdate, pH 1, followed by drying and air calcination. Then rhodium was deposited. For the 15% Mo catalysts, a dual impregnation was used to overcome solubility limitation. Before testing, catalysts were reduced in flowing H₂ at 500° [All temperatures are °C]. Performance testing was in a flow reactor system. Data were obtained at 3 MPa, H₂/CO = 2, at 3000 to 36,000 GHSV, 200° to 250°. Steady state product analysis was by on-line GC. To make comparisons, space rates were varied at constant temperature to obtain equal conversions (limited to 6%), then conversions were "normalized" to 3000 GHSV by multiplying by the factor : actual GHSV/3000. The reaction has been shown not to be mass or heat transfer limited (8). CO and irreversible H₂ chemisorption were measured at room temperature, the former using a pulse injection system and a thermal conductivity detector, and the latter using a static system. Previous to measurements, catalysts were reduced under the same schedule as for reactor runs.

RESULTS AND DISCUSSION

Catalyst composition — effect on performance. The activity of supported Rh catalysts for CO hydrogenation at 250° was found to be TiO₂-500 > TiO₂-300 > Al₂O₃ > SiO₂. For TiO₂, 500 and 300 refers to the reduction temperature used before testing. Detailed data for Rh/TiO₂ and Rh/Al₂O₃ are found in Table 1. The effect of modifiers was also studied, particularly for selectivity enhancement. In this paper, selectivity refers to the conversion of CO to oxygenates relative to hydrocarbons. The results of some of the various modifiers on the selectivity of Rh/Al₂O₃ and of Rh/TiO₂ are shown in Fig. 1. The line which is drawn for Rh/Al₂O₃, shows that selectivity decreases moderately with increasing conversion. The Mo-modified catalysts are unique in their high activities and increased selectivities (4,6,7,8,9). For instance the activity was increased 12-fold by addition of 7.5% Mo. A 4% conversion was obtained at 225° at 18,000 GHSV, and selectivity was 73%. When measured at 250°C, the % selectivity increased progressively with added % Mo : 29-0; 58-2.8; 65-7.5; 69-15, Table 1.

Molybdena added to Rh/TiO₂ was also effective in increasing activity and selectivity, Table 1.

In addition, molybdena brought a high capability for the shift-conversion reaction with as much as 25% of the converted CO going to CO₂. The amount of CO₂ observed is consistent with the reaction $\text{CO} + \text{H}_2\text{O} \longrightarrow \text{CO}_2 + \text{H}_2$ utilizing the amount of water produced from formation of hydrocarbons and higher alcohols.

Temperature — effect on catalyst performance. The rates of formation of some of the products as a function of temperature have been published previously (6) and additional data are shown in Fig. 2. The calculated values of apparent E_{act} given in Table 2 for overall CO conversion is the same for Rh/Al₂O₃ and Rh/MO/Al₂O₃. Hence higher reaction rates with the latter catalyst is not due to a lower E_{act} . It should also be noted that for the Rh-Mo/Al₂O₃ catalysts E_{act} for oxygenates as a group is 18.6 Kcal/mole, much lower than the 31.2 volume for hydrocarbons. Individual products show smaller but significant differences from these values, for example 32.4 for CH₄ and 27 for C₂H₆. The consequence is that there is a double penalty for operation at higher temperatures. Not only are hydrocarbons increased relative to oxygenates, but also the hydrocarbons consist of larger amounts of less valuable CH₄. It is also significant that $E_{\text{act, C}_2+\text{oxy.}} > E_{\text{act, C}_{1\text{oxy.}}}$. This is believed due to the circumstance that CO dissociation is required for hydrocarbons and higher alcohols but not C₁ oxygenates.

Utilizing activation energy differences for selectivity control. The wide differences in E_{act} between formation of oxygenates and hydrocarbons results in a more rapid decrease in the rate of formation of hydrocarbon relative to oxygenates as temperature is decreased. Selectivity is increased. The relative rates for selective, r_o , and non-selective, r_h , reactions are expressed by the relationship

$$\frac{r_o}{r_h} = \frac{\text{selectivity to oxygenates}}{\text{selectivity to hydrocarbons}} = D \cdot e^{\frac{-(E_o - E_h)}{RT}}$$

D is a constant whose value, $\log D = -5.60$, was established from experimental selectivities for Rh/7.5Mo/Al₂O₃. The following selectivities to oxygenates represent those calculated and found and those predicted for various temperatures.

Temp.°	273	250	225	200	180	160	140
Calculated %	50	61	75	85	91	95	98
Found %		65	73	86			

One application of this calculation is to provide a prediction of the selectivities which may be obtained with catalysts of sufficient activity to be used at lower temperatures.

The use of lower temperatures to increase selectivity has a penalty — namely loss of conversion rate. The decrease in rate can also be calculated for selective and nonselective reactions as a function of temperatures:

$$\frac{\text{rate } T_1}{\text{rate } T_2} = e^{\frac{-E(T_1 - T_2)}{RT_1 T_2}}$$

This is illustrated by the following:

	oxygenates	hydrocarbon
E_{act} cal/mole	18,600	31,200
50° decrease, 250° – 200°	7 fold	rate loss 24 fold
90° decrease, 250° – 160°	42 fold	524 fold

The above calculations can provide the initial basis for optimizing process design in which advantages of increased selectivity — improved product value, lower plant and operations costs for separation, and possible longer catalyst life — are calculated and related to disadvantages of lower rates of conversion — larger catalyst inventory and increased reactor investment. Thus an increase of selectivity from 65 to 86% for Rh/7.5%Mo/Al₂O₃ in going from 250° to 200° may more than compensate for the requirements imposed by a 7-fold increase in catalyst inventory to reach the same conversion level.

Rate comparisons with other catalysts. It is of interest to compare the space-time-yield for Rh/Mo/Al₂O₃ catalyst and industrial Cu/ZnO/Al₂O₃ catalysts. The STY for Rh/7.5%Mo/Al₂O₃ at 250° at 36,000 GHSV in g/hr/ml catalyst corresponds to 1.0 for all products, 0.76 for oxygenates and hydrocarbons, or 0.4 for oxygenate liquids (0.51 ml/hr/g). Commercial catalysts are said to produce 0.5 ml methanol/hr/ml cat. Thus the Rh/Mo/Al₂O₃ catalyst is as active as commercial catalyst. They are by far the most active of supported Rh catalysts identified in a wide survey (11).

Kinetics. The coefficients of the kinetic power-law rate expression for CO hydrogenation

$$\text{Rate}_{\text{species}} = A \cdot p_{\text{H}_2}^x \cdot p_{\text{CO}}^y$$

were determined for Rh/Al₂O₃ and Rh/Mo/Al₂O₃, Table 3 (3,6,8). A negative value for the exponent of pCO for the Rh/Al₂O₃ catalysts is interpreted to indicate that there is an inhibition of the reaction by preferential adsorption of CO relative to H₂ on the Rh. However, for the Mo-modified catalyst the exponent of pCO is zero for the overall conversion of CO, for MeOH and for CO₂ formation. While CO₂ is mechanistically a secondary product, it follows the power-law because product water is immediately converted to CO₂. Significantly, the exponent of pCO remains negative for the formation of methane and higher alcohols. This is interpreted to mean that formation of CH₄ and higher alcohols is occurring at Rh sites, and that dissociation of CO is involved which is subject to inhibition by CO. Formation of methanol does not involve CO dissociation and is not inhibited by CO.

H₂ and CO chemisorption and turnover frequency. The dispersion of Rh in the Rh/Al₂O₃ catalyst was determined to be 39%, based on H₂ chemisorption and assuming 1H/1Rh. However, for Mo catalysts, H₂ cannot be used for this purpose because of the formation of non-stoichiometric Mo bronzes. Therefore, CO was used to measure Rh dispersion for Mo catalysts. H₂ adsorption on Rh/Al₂O₃ provided an initial calibration point. It was determined that CO does not adsorb appreciably on partially reduced molybdena under the above-mentioned conditions. While CO can adsorb in different forms, as determined by infrared measurements, it is assumed that the stoichiometry of CO chemisorption on Rh does not change with increased Mo and can be used as a measure of Rh dispersion. The amount of CO chemisorbed decreased progressively and substantially with addition of molybdena, Table 4. Also shown is the overall rate of CO conversion, labelled the turn-over-frequency, for each Rh atom in the sample. The TOF shows an increase as increasing amounts of Mo are added. Thus, even though the number of CO adsorption sites decreases, the rate of CO conversion increases. Furthermore, more impressive increases are observed if the comparison is done on the TOF based on each CO adsorption site. Thus at 15% Mo, the overall activity per CO site increased by 150 fold!

CONCLUSIONS AND COMMENTS

The exponential form of the reaction rate dependence on activation energy and temperature makes rates very sensitive to activation energies and temperatures. As a consequence, differences in activation energies between selective and non-selective reactions can provide for significantly increased selectivities at lower temperatures. Decreasing reaction temperatures from 250° to 200°, for Rh-MoAl₂O₃ for example, increases selectivity to oxygenates (E_{act} 18.6 Kcal/mole) from 65% to 85% relative to hydrocarbons (E_{act} 31.2 Kcal/mole). Reaction rates are decreased 7-fold. The selectivity is predicted to increase to 98% at 160°. Changes in the distribution of individual hydrocarbons and oxygenates with reaction temperature are also predicted. Such considerations provide a preliminary basis for process optimization through temperature selection.

The greatly enhanced activity and selectivity imparted by Mo addition to Rh/Al₂O₃ is not explained by activation energy differences alone. Gilhooley, Jackson and Rigby (5) found wide variations in the apparent activation energies and pre-exponential factors for Rh on various supports. They concluded that the compensation effect, which involves the pre-exponential factor, made conclusions on mechanism ambiguous.

Examination of the power-law exponents presented here show that the rate of hydrogenation of CO to hydrocarbons and oxygenate is inhibited by CO over Rh/Al₂O₃ but not for methanol formation over Rh-Mo/Al₂O₃. Interestingly, the inhibition for CH₄ formation remains. The implication is that the mechanism of the rate determining step for methanol differs from methane and that the latter is dependent on the Rh.

Based on these results and other characterization tests (8), it is proposed that Rh-Mo/Al₂O₃ catalysts operates by a dual site mechanism in which CO is activated by Rh and hydrogen is activated by MoO_(3-x) with migration of activated hydrogen to the activated CO. A major point is that while Rh is capable of activating H₂, its activation is inhibited by CO during CO hydrogenation. In contrast, H₂ activation by MoO_{3-x} is not inhibited by CO. As a consequence of increasing the hydrogenation capability, which is rate-limiting, the overall catalytic activity for CO conversion is greatly accelerated. The increase in oxygenates is also due to increased hydrogenation ability which shows up particularly in methanol formation. The formation of hydrocarbons and higher alcohols involve CO dissociation believed to occur on Rh. As the power-law data show, their formation even over Rh-Mo/Al₂O₃ is inhibited by CO which is visualized as strongly occupying the Rh sites.

For the practical purpose of achieving higher selectivities at lower temperatures, say 160°, catalysts of increased activity are required. The results discussed here are believed to provide a guide for design of improved dual-site catalysts. The search should be for a structure which provides a H₂ activation site not inhibited by CO. It is speculated that to fulfill this role requires a non-metallic, non-stoichiometric structure such as a partially reduced oxide. For Mo catalysts there is the potential for improvements by use of unusual oxide structures, or of reduction to a MoO_{3-x} of more optimum level, or possibly by use of sulfides instead of oxides. A better knowledge of the interface of Rh and partially reduced molybdena is of great interest as well as the mobility of activated hydrogen to or from the Rh (4,8). The extremely high increase in activity, namely 150-fold, of Rh sites identified by CO chemisorption on the 15% Mo/Rh/Al₂O₃ catalyst, illustrates the possibility of catalysts with greatly increased activity. These could be used with great advantage at lower temperatures than present industrial catalyst.

ACKNOWLEDGEMENTS

Early experimental and conceptual contributions by Dr. C. Sudhakar are recognized. This work was supported by the Department of Energy Grant DE-FG22-84PC70780.

REFERENCES

1. Wilson, T.P., Kasai, P.M., Ellgen, P.C. *J. Catal.* **69**, 193-201 (1981).
2. van den Berg, F.G.A., Glezer, J.H.E., Sachtler, W.M.H. *J. Catal.* **93**, 340-352 (1985).
3. Underwood, R.P., Bell, A.T. *Applied Catal.* **21**, 157 (1986).
4. Jackson, S.D., Braneth, B. J., Winstanley, D. *Applied Catal.* **27**, 325-333 (1986).
5. Gilhooley, K., Jackson, S.D., Rigby, S. *Applied Catal.* **21**, 349 (1986).
6. Sudhakar, C., Bhore, N.A., Bischoff, K.B., Manogue, W.H., Mills, G.A. in *Catalysis 1987*, Ward J.W., Ed., Elsevier Sc. Pub. Amsterdam, 115-124 (1988).
7. Bhore, N.A., Sudakar, C., Bischoff, K.B., Manogue, W.H., Mills, G.A. in *Catalysis: Theory to Practice*, Phillips, M. J., Tiernan, M., Eds., Chem. Inst. Canada, Ottawa v. 2 594-601 (1988) v5 (1989).
8. Bhore, N.A. *Modifiers in Rhodium Catalysts for Carbon Monoxide Hydrogenation: Structure - Activity Relationships*. Ph.D. Thesis, University of Delaware, 1989.
9. Kip, J. B., Hermans, E.G.F., Van Wolput, J.M.H.C., Hermans, N.M.A., van Grondelle, J., Prins, R. *Applied Catal.* **35**, 109-139 (1987).

10. Arakawa, H., Hamaoka, T., Takeuchi, K., Matsuzaki, T., Sugi, Y. ref. 6, v 2, 602-609 (1988).
11. Klier, K. in *Coal Liquefaction — A Research & Development Needs Assessment*. DOE Contract DE-AC01-87ER30110 (1989).

Table 1. CO Hydrogenation by Catalysts of Various Compositions, $H_2/CO=2$; 3MPa.
All contain 3% Rh.

	0% MoAl ₂ O ₃		2.8% Mo Al ₂ O ₃	7.5% Mo Al ₂ O ₃				15% MoAl ₂ O ₃		6% Mo TiO ₂	
Temp.	250	275	225	200	225	235	250	200	225	225	250
GHSV	3000	3000	3000	3000	18000	18000	36000	3000	3000	4700	11230
% Conversion of CO, includes CO ₂											
Conv. to CO ₂	5.7	12.5	9.0	7.3	4.0	6.0	5.3	6.0	27	11.2	12.3
	1	1	21.5	23.9	23.0	25.6	24.5	25	37	35	38
% of CO Converted, excludes CO ₂											
CH ₄	60	69	34.8	9.4	18.4	23.8	26.8	7.2	10.6	27.4	35
C ₂ H ₆	4	4.1	4.5	3.1	5.8	4.7	5.9	2.4	4.4	11.6	15.3
C ₃ H ₈	5	5.0	1.5	1.1	2.3	1.9	2.3	0.9	1.6	4.7	5.5
C ₄ H ₁₀	2	1.4	0.4	0.3	0.6	0.5	0.6	0	0.5	1.6	2
C ₅ H ₁₂		2.0		0	0	0	0			0	0
Total HCs	71	81.5	41.7	13.9	27.1	30.2	35.6	10.5	17.1		
MeOH	2	0.8	13.4	37.6	21.7	17.7	15.7	24.0	10.9	38.9	26
MeOMe	1	0.2	15.9	30.0	28.3	26.9	26.5	39.5	56.5	3.1	4.5
MeCHO	2	2.3	0	0	0	0	0	0	0	0	0
EtOH	11	5.2	12.3	5.8	7.4	7.4	6.7	18.0	1?	7.5	6.4
MeOAc	3	2.6	2.4	1.1	1.1	0.7	0.7	0.2	0.7	2.1	1.7
HOAc	0	0	0	0	0	0	0	0	0	0	0
EtCHO	0.4	0	0	0	0	0	0	0	0	0	0
C ₃ H ₇ OH	2.7	2.5	2.4	1.9	0.9	2.2	0.7	2.4	2.7	1.4	1.2
MeOEt	3	21.	12.6	9.9	14.0	14.5	14.5	7.0	11.2	3.0	2.5
EtOAc	3	3.6	0	0	0	0	0	0	0	0	0
C ₄ H ₉ OH	0	0.6	0	0	0	0	0	0	0.4	0	0
Total Oxy.	28.9	18.9	58.7	86.3	73.3	69.2	64.8	90	83	56	39
C _{1oxy.}	5.1	2.6	34.3	71.4	55.0	49.6	47.3	65.9	71.3	43.6	30.8
C _{2oxy.}	20.7	14.2	22.2	13.0	17.4	17.4	16.8	22.8	8.9	10.9	8.6
C _{3oxy.}	3.0	2.5	2.4	1.9	0.9	2.2	0.7	2.4	2.6	1.4	1.2
C _{2+oxy.}											
% of oxy.	82.4	86.2	41.6	17.2	21.7	28.1	26.7	27.7	14.0	19	21

Table 2. Apparent Activation Energies, CO Hydrogenation

	Product	Kcal/g mol
3% Rh/Al ₂ O ₃ 3% Rh/7.5% Mo/Al ₂ O ₃	-CO	21.3 ± 0.3
	-CO	21.6 ± 0.9
	C _{1oxy}	17.2 ± 0.7
	C _{2oxy}	24.3 ± 2.4
	<u>C_{total oxy}</u>	<u>18.6 ± 0.9</u>
	CH ₄	32.3 ± 2.6
	C ₂ H ₆	27.5 ± 3.6
	C ₃ H ₈	28.6 ± 4.1
	C ₄ H ₁₀	26.3 ± 2.9
	<u>C_{total HC}</u>	<u>31.2 ± 2.5</u>
	CO ₂	21.9 ± 0.7

Table 3. Power Law Coefficients for CO Hydrogenation Rate_{species} = A · p_{H₂}^x · p_{CO}^y

Catalyst	Species	x	y
3%Rh/Al ₂ O ₃ 3%Rh-15%Mo/Al ₂ O ₃	-CO	0.8	-0.3
	-CO	0.72 ± 0.05	-0.03 ± 0.09
	+CH ₄	1.02 ± 0.08	-0.32 ± 0.09
	+CH ₃ OH	1.53 ± 0.01	-0.01 ± 0.11
	+C ₂ +oxy.	0.91 ± 0.23	-0.47 ± 0.23
	+CO ₂	0.38 ± 0.05	-0.04 ± 0.06

Table 4. CO Chemisorption and Site Reactivity (TOF) as Function of Mo in 3%Rh,x%Mo/Al₂O₃.

Wt% Mo	CO Chemisorption μ moles/g	% Dispersion of Rh	#CO Reacted/site-sec.**	
			per atom Rh	per site Rh***
0	112	39*	0.4	1
2.8	74	26	4.0	15
7.5	46	16	8.0	50
15.0	28	10	15.0	150

* Determined by H₂ chemisorption.

** CO Hydrogenation at 225°.

*** Per CO site.

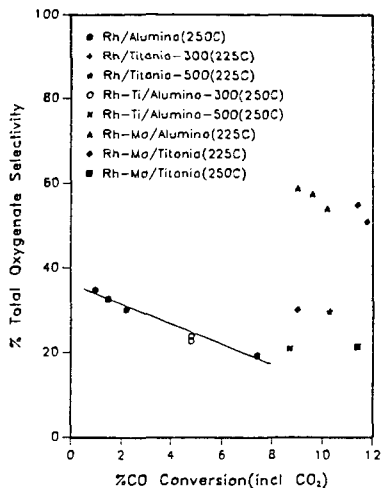


Figure 1. Effect of Catalyst Composition and Conversion Level on Selectivity to Oxygenates. 3%Rh on Al_2O_3 or on TiO_2 Modified by 1 Atom Mo or Ti per Atom Rh. CO Hydrogenation 3MPa, $\text{H}_2/\text{CO}=1$, Various Space Rates (Run Temp. $^{\circ}\text{C}$).

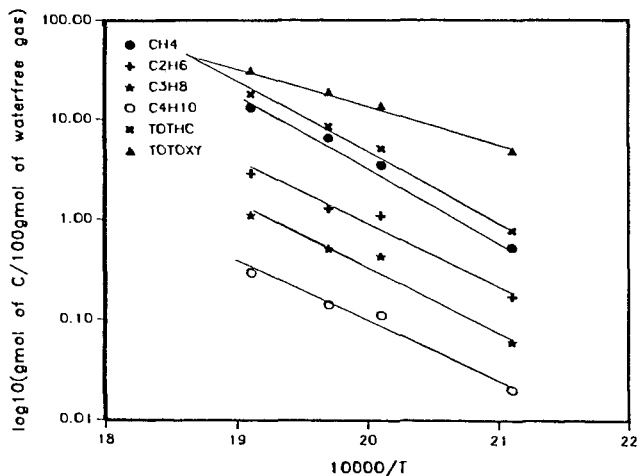


Figure 2. Rates of Formation of Hydrocarbons and Total Oxygenates Over 3%Rh/7.5%Mo/ Al_2O_3 . 3MPa $\text{H}_2/\text{CO}=1$. Rates Normalized to 3000 GHSV. See Table 2 for E_{act} .